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CONCENTRATIONS OF LEGACY AND EMERGING FLAME RETARDANTS IN AIR AND SOIL ON A TRANSECT IN THE UK WEST MIDLANDS

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Abstract

Passive air samples were collected monthly for 6 months from 8 sites along a transect of Birmingham, United Kingdom between June 2012 and January 2013. Soil samples were collected once at each site. Average concentrations of BDE-209, $\Sigma PBDEs_{17:183}$ and ΣPBDEs in ambient air were 150, 49, and 180 pg m^{-3}, respectively. Atmospheric concentrations of PBDEs were negatively correlated with distance from the city centre, exhibiting an "urban pulse". The average ΣHBCDD air concentration was 100 pg m^{-3}, however concentrations were not correlated with distance from the city centre. Several emerging flame retardants (EFRs) were identified in air and/or soil samples: 2,3,4,5-tetrabromo-bis(2-ethylhexyl) phthalate (BEH-TEBP), 1,2-dibromo-4-(1,2 dibromoethyl)cyclohexane (TBECH or DBE-DBCH), allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), decabromodiphenyl ethane (DBDPE), and dechlorane plus (DP or DDC-CO). Average concentrations of BDE-209, $\Sigma PBDEs_{17:183}$ and ΣPBDEs in soil were 11, 3.6, and 15 ng g^{-1} soil organic matter. PBDE concentrations in soil were higher at sites closest to the city centre, however correlations with distance from the city centre were not significant. BDEs-47 and -99 contributed more to ΣPBDEs in soil samples than air samples, but in both, the predominant congener was BDE-209. BATE was more abundant in air than soil but ATE was abundant in soil but not air.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have been used extensively as flame retardants in textiles, plastics and electronic and electrical equipment. Concerns over their potential toxic nature have led to bans on Penta- and Octa-BDE technical products within Europe in 2003, and globally under the UNEP Stockholm Convention (SC) in 2009 (Stockholm Convention, 2009). Significant restrictions have been put on the DecaBDE technical product since 2008 (Deffree, 2008) and HBCDD was listed under the SC in 2013 (Health and Environment Alliance, 2013).

Previous studies of PBDEs in outdoor air along rural-urban transects of cities in Canada (Gouin et al., 2005; Harner et al., 2006; Melymuk et al., 2012) the UK (Harrad and Hunter, 2006), Australia (Hearn et al., 2012) and Sweden (Newton et al., 2015) have found an "urban pulse" of higher concentrations within the city, decreasing with distance from the city centre. This urban pulse was also seen in soil samples in the UK study (Harrad and Hunter, 2006). Higher PBDE concentrations have been found in indoor air than outdoor air (Harner et al., 2006; Newton et al., 2015) and recent studies have shown that indoor air released via ventilation systems is a major pathway for outdoor air contamination with PBDEs (Björklund et al., 2012; Newton et al., 2015). Thus, the urban pulse for PBDEs seems to be directly linked to the higher density of buildings within a city, which contain flame-retarded goods that emit PBDEs to the indoor environment and subsequently to outdoor air. The possible urban pulse behaviour of HBCDDs has not been studied and measurements in urban outdoor air samples are limited (Remberger et al., 2004; Hoh and Hites, 2005; Abdallah et al., 2008; Yu et al., 2008; Takigami et al., 2009; Hu et al., 2011; Li et al., 2012)

PBDEs and HBCDDs are being replaced by a number of emerging flame retardants (EFRs). Firemaster® 550 has been used widely as a replacement for PentaBDE and contains 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), and triphenyl phosphate(TPhP)(Stapleton et al., 2008). Potential replacements/substitutions also include: bis(2,4,6-tribromophenoxy) ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) for OctaBDE and DecaBDE respectively. Other EFRs in use include dechlorane plus (DP or DDC-CO), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH or DBE-DBCH), allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), hexabromobenzene (HBB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE or TBP-DBPE) and pentabromotoluene (PBT) (Covaci et al., 2011; Bergman et al., 2012).

A number of EFRs have been found in outdoor air (Hermanson et al., 2010; Möller et al., 2010; Möller et al., 2011a; Möller et al., 2011b; Salamova and Hites, 2013; Salamova et al., 2014) and deposition samples (Meyer et al., 2012; Newton et al., 2014) from remote sites in the Arctic. HBCDDs have also been found in several air and deposition samples from the Arctic (Remberger et al., 2004; de Wit et al., 2010) (Hermanson et al., 2010; Meyer et al., 2012). This indicates that these FRs are released to the atmosphere from source regions and undergo long range atmospheric transport to the Arctic. Thus it may be that EFRs and HBCDDs in indoor air behave similarly to PBDEs and are emitted from flame-retarded products to indoor air and released from buildings to the outdoor environment. If this is the case, they should also show an urban pulse similar to that found for PBDEs. In support of this, Newton et al.(2015) recently found an urban pulse in outdoor air for several EFRs (DBDPE, EH-TBB, PBT, α– and β-DBE-DBCH) in Stockholm, Sweden. However, concentrations of many EFRs were below the detection limits and their atmospheric

behaviour could therefore not be determined. Higher PBDE and HBCDD concentrations have been observed in UK compared to Swedish indoor environments (Harrad et al., 2010), and we hypothesise this will also be the case for EFRs. Thus, if HBCDD and EFRs are escaping from indoor environments to outdoor air from buildings, their atmospheric concentrations may be higher in Birmingham than Stockholm. The aim of this study was therefore to investigate the role of a city centre (Birmingham, UK) on concentrations of HBCDDs and EFRs in outdoor air and soil along a transect in the West Midlands conurbation of the UK, of which Birmingham is the major city. PBDEs were included for comparison with a previous such study carried out in 2003/2004 (Harrad and Hunter, 2006) in order to evaluate their response to the bans in 2003 (Penta- and OctaBDE) within the EU. BDE-209 is also included to evaluate its behaviour in outdoor air for this congener related to the use of the DecaBDE formulation. To our knowledge this study presents the first ambient air and soil data on EFRs for the UK.

2. Materials and Methods

2.1 Sampling & Site Selection

Eight sampling sites were located on a 60 km transect along the prevailing wind direction from the south-west, through the city of Birmingham, to the north-east of the West Midlands conurbation (Figure 1, Table S1, Supporting Information (SI)) and reflected varying degrees of urbanisation (i.e. building density). Outdoor passive air samples (PAS) were collected monthly from each location between June 2012 and January 2013 (Table S2, SI) using the same configuration previously developed (Abdallah and Harrad, 2010).

Each PAS consisted of a polyurethane foam (PUF) disc (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) and a glass fibre filter

((GFF) 125 mm diameter, 1 μm pore size, Whatman, UK) as the sampling media. This configuration (Figure S1, SI) samples both the gaseous and particulate phases, thereby facilitating detection of higher molecular weight compounds such as BDE-209, and other compounds including HBCDDs, which are present in both phases (Harrad and Abdallah, 2008; Abdallah and Harrad, 2010). This is important as if only the vapour phase was sampled concentrations of such compounds would be underestimated. The PUF disk and filter are sheltered between two stainless steel housings (top housing - 23 cm diameter, two litre volume; and bottom housing - 18 cm diameter, one litre volume). The GFF is suspended in the middle of the sampler, supported by a wire mesh. The sampler was designed so that air would flow over the GFF and the particulate phase would be sampled by the upper face of the GFF by a combination of gravitational settling and turbulent deposition. The GFF was lost from site 5 (Edgbaston) during sampling period 3 and so no BDE-209 data were available for that particular sample.

Soil sampling was performed at each site in January 2013 using the method of Evans (2007). Briefly, three sub-samples were taken at each location, at least 1 metre apart within a 1 m^2 area from the top 5 cm of surface soil and were transferred using a stainless steel trowel into (dichloromethane (DCM) and *n*-hexane pre-rinsed) amber jars on site. The sub-samples were combined, sieved (<2 mm), homogenised, and stored at <4°C prior to extraction.

2.2 Extraction and Clean-up

Target compounds were extracted from PAS (PUF and GFF from each sample combined) at the University of Birmingham (UB) using pressurised liquid extraction (PLE). Samples were concentrated to near dryness and reconstituted in 100 μL methanol. Full extraction parameters are provided as supplementary material. The final extract was sonicated for 30 s

and transferred to an inserted autosampler vial. After analysis via LC -MS/MS for HBCDDs and BDE-209, sample extracts were reconstituted in *n*-nonane for PBDE analysis via GC-EI/MS.

The extracts underwent further clean-up and fractionation for EFRs at Stockholm University (SU) as previously described (Sahlstrom et al., 2012; Newton et al., 2015) . Further detail is provided as supplementary material.

PBDEs were extracted from soil samples via complete in-cell extraction and clean-up at UB as previously described (Abdallah et al., 2013). More details are provided as supplementary material. The final volume was adjusted to 100 µL in methanol. The sample was sonicated for 30 s and transferred into an inserted vial and analysed for BDE-209 via LC-APPI-MS/MS. The sample was then solvent exchanged into 50 µL in *n*-nonane before analysis of tri-hepta PBDEs via GC-EI/MS. Organic matter (OM) content in soil samples was determined (gravimetrically) as the loss on ignition after heating the dried samples at 500 °C for 4 h.

A separate aliquot of 10 g of soil was taken for extraction, fractionation and analysis of EFRs and HBCDDs at SU. ^{13}C-labelled BDEs -155, -183, -197, and -209, DDC-CO *syn*, DDC-CO *anti*, α-, β-, and γ-HBCDD and $^{13}C_6{}^2H_{17}$-labelled EH-TBB and BEH-TEBP were used as surrogate standards. Samples were mixed with 8 mL water and 40 mL acetone, rotated on a mechanical rotator for 60 minutes, centrifuged and the supernatant was poured into a separation funnel containing 50 mL 0.2 M NaCl/0.1 M H_3PO_4. The soil samples underwent a second extraction in 40 mL of 3:1 *n*-hexane:acetone, rotation for 60 minutes, centrifugation and the supernatant was combined with that from the first extraction. Phases were allowed to

166 separate and the organic phase was removed. The aqueous phase was washed twice with 10
167 mL *n*-hexane:diethylether (90:10). Samples were then solvent-exchanged to isooctane and
168 the volume adjusted to approximately 2 mL. To remove sulfur, 2 mL 2-propanol, 2 mL
169 TBA-reagent (tetrabutyl-ammonium hydrogen sulfate solution saturated with sodium sulfite)
170 and one tip of a spatula of sodium sulfite were added to the samples. They were then shaken
171 vigorously in a 50 °C water bath. 6 mL MilliQ water was added, samples were centrifuged,
172 and the organic phase removed. Sample extracts then underwent the same fractionation and
173 clean-up as described for air samples, with the addition of a third fraction eluted with 10 mL
174 50:50 diethyl ether:*n*-hexane which contained HBCDDs (Sahlstrom et al., 2012).

175 *2.3 Instrumental Analysis*

176 Analysis of PBDEs in all air and soil samples and HBCDDs in air samples was performed at
177 UB. Tri-heptaBDEs were determined via GC-EI/MS using an Agilent 5975 MS coupled with
178 an Agilent 6850 GC with an Agilent DB-5ms column (30 m x 0.25 i.d. x 0.25 µm film
179 thickness) (Drage et al., 2014). BDE-209 (all samples) and HBCDDs (air samples only) were
180 analysed using LC-MS/MS. Full methods and temperature programmes can be found
181 elsewhere (Abdallah et al., 2007; Abdallah et al., 2009; Drage et al., 2014) .
182
183 Analysis of HBCDDs in soil samples and EFRs in all air and soil samples was performed at
184 SU. EFR analyses for fractions 1 and 2 were performed using a Trace GC Ultra fitted with a
185 15 m TG-5HT column (Thermo Scientific, Waltham, USA, 0.25 mm i.d., 0.1 µm film
186 thickness) except BEH-TEBP for which a 30 m TG-5SILMS column was used (Thermo
187 Scientific, Waltham, USA, 0.25 mm i.d., 0.25 µm film thickness, see QA/QC section below
188 for further explanation). The GC was coupled to a DSQ II MS (Thermo Scientific, Waltham,
189 USA) operating in ECNI mode with ammonia as the moderating gas. HBCDDs were
190 measured using ultra performance LC (ACQUITYTM UPLC) coupled to a tandem-

quadrupole MS (Xevo™ TQ-S). A UPLC column (ACQUITY UPLC® HSS C18; 1.8 µm; 2.1×100 mm), with a pre-column (ACQUITY UPLC™ HSS C18; 1.8 µm VanGuard™; 2.1× 5 mm) was used for separation. Temperature programs and other instrumental parameters can be found elsewhere (Sahlstrom et al., 2012).

2.4 Quality Assurance/Quality Control

PAS were calibrated against active samplers for some PBDEs to determine the volume of air sampled and therefore the estimated concentrations (pg m^{-3} air). The calibration used the same basic method as that used by Abdallah and Harrad (2010) for indoor air. Further information about how passive sampling rates were calculated is provided as supplementary material.

PUF disks were pre-extracted via PLE (ASE-350 (Dionex)) with 3:2 DCM:hexane (90°C and 1500 psi; flush time – 5 minutes; static cycle – 4 minutes; purge time – 120 s; 1 static cycle). GFFs were baked for 5 hours at 500 °C before the samplers were assembled and deployed. Shelters were also thoroughly rinsed with n-hexane and acetone before each sampling period to avoid potential cross-contamination. The inner surface of the top housing of the PAS was coated with aluminium foil and washed with n-hexane and acetone to try to minimise its particle-scavenging potential (Abdallah and Harrad, 2010). PAS housing and PUFs were cleaned within one day of being deployed and were subsequently stored and transported to sampling sites in sealed plastic bags. One field blank was analysed with every five samples, which consisted of one pre-extracted PUF and one GFF, stored in an airtight sealed bag for the sampling campaign. The method limit of detection (mLOD) was defined as the average blank level plus 3 standard deviations for compounds present in the blanks. In general, blanks did not contain target compounds. However, BDE-209 was detected in the majority of blanks at a level below 5% of all samples within the batch. Unstable ion ratios between the

quantifying and qualifying ions for BEH-TEBP (383.8 and 463.7, respectively) were observed. To rectify this, samples were rerun on a 30 m column to separate possible interferences and 512.9 was used as a qualifying ion, which resulted in less variability of ion ratios. For positive detection, ion ratios were allowed to deviate no more than 20% from the average ratio measured in the standards. Further to these criteria, recoveries of isotopically labelled internal standards were required to be between 25% – 150% for a value to be reported. The average recoveries of internal standards were 55% (^{13}C-BDE-28), 68% (^{13}C-BDE-47), 79% (^{13}C-BDE-99), 53% (^{13}C-BDE-153), 87% (^{13}C-BDE-209) 52% (^{13}C-DDC-CO *syn*), 38% (^{13}C-DDC-CO *anti*), 41 % (^{13}C-α-HBCDD), 73% (^{13}C-β-HBCDD) and 63% (^{13}C-γ-HBCDD).

All descriptive statistics were performed using Microsoft Excel 2007 or 2010, with statistical tests processed through SPSS for Windows (version 19.0 or 20). For statistical purposes, non-detects were replaced with zero. All confidence limits were set to 95% (p = 0.05).

3. Results and Discussion

Mean concentrations of PBDEs, HBCDDs, and EFRs in air (pg m^{-3}, total concentrations) and concentrations in individual soil samples (pg g^{-1} OM) are given in Tables 1 and 2, respectively. Concentrations for individual air samples from each site as well as sampling rates (pg day^{-1}) are given in Tables S4-S6 (SI).

3.1. Spatial variability in Ambient Air

PBDEs

BDE-209 was detected in measurable concentrations in the majority of samples (39 out of 48), highlighting its extensive use in the UK (Table S4, SI). At each site, BDE-209 comprised

241 61-92% of ΣPBDE (ΣPBDE = sum of BDEs -17, -28, -47, -49/71, -66, -85, -99, -100, -153, -
242 154, -183, -209). Surprisingly, the highest ΣPBDE concentrations were found in Bromsgrove
243 (site 3, a suburban site 20 km southwest of the Birmingham city centre) with an average of
244 490 pg m^{-3} (92% BDE-209), more than double the concentrations of the most urban sites of
245 Digbeth and Edgbaston (sites 6 and 5, 180 and 210 pg m^{-3} respectively). However, the mean
246 concentration at Bromsgrove is skewed by one sample (June-July which contained 1500 pg
247 BDE-209 m^{-3}). There are no known sources of PBDEs close to the Bromsgrove sampling site,
248 such as chemical companies or industries using thermal processes such as steel
249 manufacturing or waste incineration.
250
251 After Bromsgrove, the highest ΣPBDE air concentrations found were close to the
252 Birmingham city centre in Digbeth, Edgbaston and Bournville (averages of 210, 170 and 180
253 pg m^{-3}) which are approximately 0, 6, and 8 km from the city centre respectively. With
254 Bromsgrove excluded, mean concentrations of BDE-209, $\Sigma PBDEs_{17:183}$ ($\Sigma PBDEs_{17:183}$ = sum
255 of BDEs -17, -28, -47, -49/71, -66, -85, -99, -100, -153, -154, -183), and ΣPBDEs were more
256 elevated close to the city centre (Digbeth, site 6) than they were further away. Correlations
257 between concentrations and distance from the city centre during each individual sampling
258 period were rarely statistically significant. However, when averaged over the full 6 months
259 sampling period, significant negative correlations between concentrations in air and distance
260 from the city centre were observed for BDE-209, $\Sigma PBDEs_{17:183}$, and ΣPBDEs ($r = -0.842$, -
261 0.872, -0.946; $p = 0.018$, 0.011, and 0.001; respectively; Bromsgrove excluded; Figure 2a).
262 This is likely due to wide month-to-month variation (see section 3.2). These correlations
263 confirm that the West Midlands conurbation is a source of PBDEs to the environment.
264

265 The strength of this pulse was calculated previously as the ratio of the sum of concentrations
266 in Birmingham city centre to the average sum of concentration of all sites (Harrad and
267 Hunter, 2006). Ratios for our study were 0.87 for BDE-209, 2.2 for $\Sigma PBDEs_{17:183}$, and 1.1 for
268 ΣPBDEs. With Bromsgrove excluded, the pulse is stronger, 1.2, 2.1, and 1.4 for BDE-209,
269 $\Sigma PBDEs_{17:183}$, and ΣPBDEs, respectively. It is unknown why the strength of the pulse for
270 BDE-209 was lower in this study than it was for the lower brominated congeners, however it
271 may be due to the proximity of domestic buildings to sampling sites. DecaBDE has been used
272 extensively in the UK to meet strict flame retardancy regulations for furniture (Harrad et al.,
273 2008). Using the same congeners as previously (2006), a ratio of 2.0 was found for
274 $\Sigma PBDEs_{28:154}$, similar to the value of 2.2 calculated previously along a similar (but not
275 identical) transect.
276
277 Concentrations of PBDEs in air in this study exceed slightly those found previously in
278 Birmingham (Harrad and Hunter, 2006) and Toronto in 2000-2001 (Harner et al., 2006).
279 Mean concentrations of ΣBDEs -47, -99, -100, -153, and -154 at each site in the current study
280 ranged from 5.8-49 pg m^{-3} compared to 2.8-23 pg m^{-3} in the previous Birmingham study.
281 $\Sigma PBDEs_{17:183}$ ranged from 5.4 to 57 pg m^{-3}, which were slightly higher, especially at urban
282 sites, than those found in Toronto in 2000-2001, which ranged from about 10-30 pg m^{-3}
283 (Harner et al., 2006). However, the largest increases in concentration between the current
284 study and the previous two studies in Birmingham and Toronto were seen for BDEs-153 and
285 -154 whereas concentrations of BDE-47 were often lower in this study (range from 1.6-7.9 pg
286 m^{-3} in the current study compared to 1.6-14 pg m^{-3} in the previous Birmingham study). This
287 could be due to the use of a GFF in the sampler used in the current study (thereby more
288 efficiently sampling the less volatile BDEs-153 and -154), or because atmospheric half-lives
289 of BDEs-153 and -154 may be longer than BDE-47. Compared to a more recent study using

high-volume samplers in Stockholm, Sweden, concentrations of BDEs-47 and -99 in Birmingham were one to two orders of magnitude greater and BDE-209 concentrations were about three orders of magnitude greater (Newton et al., 2015). For congeners measured in both studies (BDEs-47, -99, -100, -153, -154, and -209), this study found a much higher contribution from BDE-209 to ΣPBDEs (88%) than Stockholm (11%). By comparison, the Stockholm study saw a much larger contribution from lower brominated PBDEs like BDE-47 (40% compared to 2.8% in Birmingham). This suggests substantially greater use and emissions of the DecaBDE formulation in the UK than in Sweden.

HBCDDs

HBCDDs were detected in the majority of air samples (44 out of 48) at similar levels to PBDEs when applying the same sampling rate for BDEs -99 and -100 (3.92 m^3 day^{-1}, Table 1, Tables S5-S6, SI). Mean ΣHBCDD concentrations in air showed slightly increased levels near the city centre (Digbeth, site 6) compared to upwind rural/suburban sites (sites 1-4) but concentrations were not correlated with distance from the city centre (Figure 2a). This is likely due to sampling at several of the sites being in proximity to buildings possibly containing HBCDDs, which was heavily used as a flame retardant in building insulation. Very little spatial variation in isomer profiles was apparent. The ΣHBCDD concentration at the Edgbaston site (site 5, average = 84 pg m^{-3}, December to January = 230 pg m^{-3}) was about twice that measured by Abdallah et al. (2008) using active sampling in December 2007 (37 pg m^{-3}) at the same site with this study displaying a considerably higher contribution from the α-isomer. The higher concentrations found in the current study could be due to ongoing emissions as no restrictions were placed on HBCDDs between the two studies. Alternatively, it may be attributed to differences in the two air sampling methods used, or to seasonal variations in atmospheric HBCDD concentrations; as the current study covers warmer

periods when concentrations of many POPs are known to be higher. The geometric mean ΣHBCDD concentration (100 pg m^{-3}) was more than three orders of magnitude greater than that measured recently in Stockholm, Sweden (0.066 pg m^{-3}) (Newton et al., 2015). Concentrations of HBCDDs in air were similar to those of BDE-209. Given its recent listing under the Stockholm Convention (Health and Environment Alliance, 2013), HBCDD should be further monitored.

EFRs

Five EFRs were identified in air samples: BEH-TEBP, DDC-CO, DBE-DBCH, BATE, and DBDPE. Compounds sought but not detected were ATE, TBP-DBPE, HBB, DBHCTD, OBTMPI, PBT, TBCO, EH-TBB, and BTBPE. BEH-TEBP and DBDPE were detected in 33% and 50% of air samples, respectively; however they were not quantified due to low recovery of the relevant internal standards (^{13}C-BTBPE and ^{13}C-BDE-209) after the additional clean-up procedure that was performed for EFRs. ΣDDC-CO (sum *syn-* + *anti-*DDC-CO) was identified in 44% of samples with no spatial trends or discernible pattern in isomer ratios. Mean concentrations of ΣDDC-CO at each site ranged from 0.57-21 pg m^{-3} (using the BDE-209 sampling rate as DDC-CO is expected to be particle bound). These concentrations are comparable to several measurements around the world including the Great Lakes (0.2-4 pg m^{-3},Venier and Hites, 2008) urban and rural areas of China (3.5-66 pg m^{-3}, Ren et al., 2008) and global background levels from the Arctic to Antarctica (0.05 - 4 pg m^{-3}, Möller et al., 2010). BATE and DBE-DBCH were detected in 77 % and 79 % of samples, respectively, with the highest levels of each found at Bournville (site 4), near a home which was completely refurbished shortly before sampling began (Figure S3, SI). A significant negative correlation with distance from site 4 was observed for DBE-DBCH ($r=-0.726$, $p=0.041$) but not for BATE (Figure 2b). BATE concentrations were higher (0.86-17 pg m^{-3},

median = 2.9) than those found at five sites in the Great Lakes region of the US using high-volume samplers (0.012 – 3.9 pg m^{-3}, medians = 0.031 – 0.092 pg m^{-3}, Ma et al. 2012). Concentrations of DBE-DBCH were 10-20 times higher (median = 7.2 pg m^{-3}) than those found by high-volume sampling at several sites in Stockholm, Sweden (0.46 pg m^{-3}) (Newton et al., 2015).

3.2 Soils

PBDEs

Concentrations of PBDEs in soils (Table 2), expressed on an OM-normalised basis, follow a similar pattern to those in ambient air. The lowest ΣPBDE concentrations were found in the sites furthest from Birmingham city centre (Worcester (3.6 ng g^{-1} OM) and Droitwich (2.3 ng g^{-1} OM)), and the highest ΣPBDE concentration (besides Bromsgrove) was found in Digbeth (21 ng g^{-1} OM – centre of Birmingham). The elevated ΣPBDE concentration found in soil from Bromsgrove (49 ng g^{-1} OM) is consistent with the higher ambient air concentrations from the same location discussed above.

The soil samples were dominated by BDE-209, but displayed slightly higher contributions of BDE-47 and BDE-99 than in air (Figure 3). The mean contribution of BDEs -47 and -99 to total PBDE content increased from 2.4% and 2.0% in air to 7.9 and 8.1% in soil, respectively, while the contribution of BDE-209 decreased slightly (77% in air vs 72% in soil). This may be due to soil reflecting a longer term integral of releases of PBDEs to the environment as well as longer half-lives of PBDEs in soil than air (Palm et al., 2002), meaning that historic releases of lower brominated congeners prior to their bans are more likely reflected in soil concentrations. Furthermore, atmospheric half-lives of BDEs -47 and -99 (10 and 20 days

364 respectively), are considerably shorter than that of BDE-209 (318 days) meaning the former
365 pair are likely to represent a lower proportion of total PBDE content in air (Palm et al., 2002).
366
367 While the relationship between concentrations in soil and distance from the city centre are not
368 statistically significant ($r = -0.518$, $p= 0.234$ for BDE-209; $r= -0.583$, $p= 0.169$ for
369 $\Sigma PBDEs_{17:183}$; $r = -0.568$, $p= 0.184$ for $\Sigma PBDEs$), urban pulses in soil are suggested.
370 Calculated in the same way as for air, and based on concentrations normalised to organic
371 matter, these pulse ratios were: 1.4, 1.8, and 1.5 for BDE-209, $\sum PBDEs_{17:183}$, and $\sum PBDEs$,
372 respectively, with Bromsgrove included; and 3.2, 1.9, and 3.7, respectively, with Bromsgrove
373 excluded. These urban pulses for soil, combined with the significant declines in air
374 concentrations with increasing distance from the city centre, are consistent with the behaviour
375 of an "urban pulse" of PBDEs (Harner et al., 2006; Harrad and Hunter, 2006).
376
377 Soil collected from the Edgbaston site had six times lower $\Sigma PBDEs_{28:154}$ concentrations (2.9
378 ng g^{-1} OM) than a soil sample taken from the same location in 2004 (19 ng g^{-1} OM) (Harrad
379 and Hunter, 2006). The decrease in concentrations during this time period is consistent with
380 a study of Scottish soils which found increasing concentrations of BDEs-47 and -99 from
381 1990-1999 but decreasing levels from 1999-2009 (Zhang et al., 2014). The authors attributed
382 the observed trends to legislation banning the use of PentaBDE. This explanation may also be
383 applicable to the differences observed between the BDE-47 concentrations in soil in this
384 study (2013) and the soils from 2004 as well as the lower concentrations observed for BDE-
385 47 in air discussed previously. However, given the heterogeneous nature of soil, more data
386 are required to draw firm conclusions.
387

388 Concentrations as well as congener patterns of PBDEs in soils were roughly comparable to
389 those reported in Stockholm recently (Newton et al., 2015). BDE-47 and -99 concentrations
390 ranged from 0.58-2.1 and 0.55-1.6 ng g^{-1} OM, respectively, compared to 0.24-1.7 and 0.20-
391 1.7 ng g^{-1} OM in Stockholm. BDE-209 concentrations ranged from 0.94-45 ng g^{-1} OM
392 compared to 0.31-31 ng g^{-1} OM in Stockholm. The comparability between concentrations
393 and congener patterns of PBDEs in soils in these two studies is in contrast to the findings in
394 air, which were 1-3 orders of magnitude higher in Birmingham than Stockholm and exhibited
395 very different congener patterns. This observation is consistent with the hypothesis that soil
396 reflects a longer time period in terms of releases of PBDEs to the environment as well as to
397 longer half-lives of PBDEs in soil than air.
398
399 *EFRs*
400 HBCDDs were found in all soil samples but were not quantified due to low recovery of the
401 surrogate standards. BATE, which was found in most air samples, was found in soil only at
402 site 8, Tamworth with a concentration of 0.049 ng g^{-1} OM. However, a related compound
403 (ATE) was found in all soil samples (Table 2). BATE and ATE are structurally related to
404 DPTE (Ma et al., 2012) and are suspected to be biotransformation products of this compound
405 (von der Recke and Vetter, 2007). These are the first reported levels of ATE in soil that the
406 authors are aware of. DDC-CO and DBDPE were each found in all but one soil sample.
407 BEH-TEBP and DBE-DBCH were not detected in soil. No significant correlations were
408 found between soil and air for any EFRs nor were they significantly correlated with distance
409 from the city centre. Median DBDPE concentrations (0.34 ng g^{-1} OM) were in the lower
410 range of those reported in Stockholm, Sweden (median of 0.91 ng g^{-1} OM) (Newton et al.,
411 2015). DBDPE concentrations on a dry weight basis ranged from <0.0059-0.24 ng g^{-1} which

were within the range reported in sediments from the Great Lakes (0.11-2.8 ng g^{-1} (Yang et al., 2012)) but much lower than agricultural soils in China (12-344 ng g^{-1} (Zhu et al., 2014)).

3.3 Seasonal Variability in ambient air

PBDEs

Significant correlations between $\Sigma PBDE_{17:183}$ concentrations and average temperature (supplied by the UK Met Office, Figure S5), were not seen, however some seasonal observations were made. The previous study of West Midlands (Harrad and Hunter, 2006) also did not find any significant seasonal trends in $\Sigma PBDE_{28:154}$ concentrations. However, they did observe spring and summer increases in BDE-47 at sites close to the city centre, which was observed in this study also. As correlations between temperature and concentrations would indicate that secondary emissions from soils are a major source to the atmosphere, the lack of correlations, coupled with evidence of an urban pulse, indicate that ongoing primary emissions from consumer products are currently a more important source to the atmosphere than secondary emissions.

A tendency was seen for BDE-209 levels in air to be lower in warmer periods at Worcester, Droitwich, Bournville, Edgbaston, Digbeth, and Tamworth (Figure S6, SI). However, this was only statistically significant for Digbeth ($r = -0.905$, $p = 0.013$). This was also observed recently in Beijing, China, by Shi et al. (2013), who found BDE-209 concentrations in outdoor air to be more variable and overall lower in the spring and summer than autumn and winter. A potential explanation for this could be the photolytic debromination of BDE-209 as shown by Da Rosa et al. (2003) under laboratory conditions.

EFRs and HBCDDs

General trends of increasing concentrations with temperature were observed for DBE-DBCH and BATE. For individual sites, no correlations were statistically significant with the exception of BATE at site 4, Bournville ($r=0.939$, $p = 0.006$) and site 7, Sutton Coldfield ($r=0.933$, $p = 0.007$). However, when concentrations from all sites were averaged, BATE concentrations were strongly positively correlated with temperature ($r=0.874$, $p=0.023$, Figure S7, SI). DBE-DBCH and ΣEFR (ΣEFR = α-DBE-DBCH + β-DBE-DBCH + BATE + DDC-CO *syn* + DDC-CO *anti*) showed higher concentrations in summer than winter but correlations with temperature were not significant (Figure S7, SI). No seasonal trends or correlations with temperature were observed for concentrations of HBCDDs, however, the contribution of α-HBCDD to ΣHBCDDs increased steadily from 35% in July to 66% in December. This may be because of the higher volatility and lower octanol-air partition coefficient (K_{OA}) of α-HBCDD relative to β- and γ-HBCDD (Marvin et al., 2011), favouring partitioning to air even at lower temperatures.

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Supplementary material

Additional description of sampling methods and locations, extraction and clean-up methodologies, individual sample ambient air concentrations for target compounds and figures demonstrating correlations and trends.

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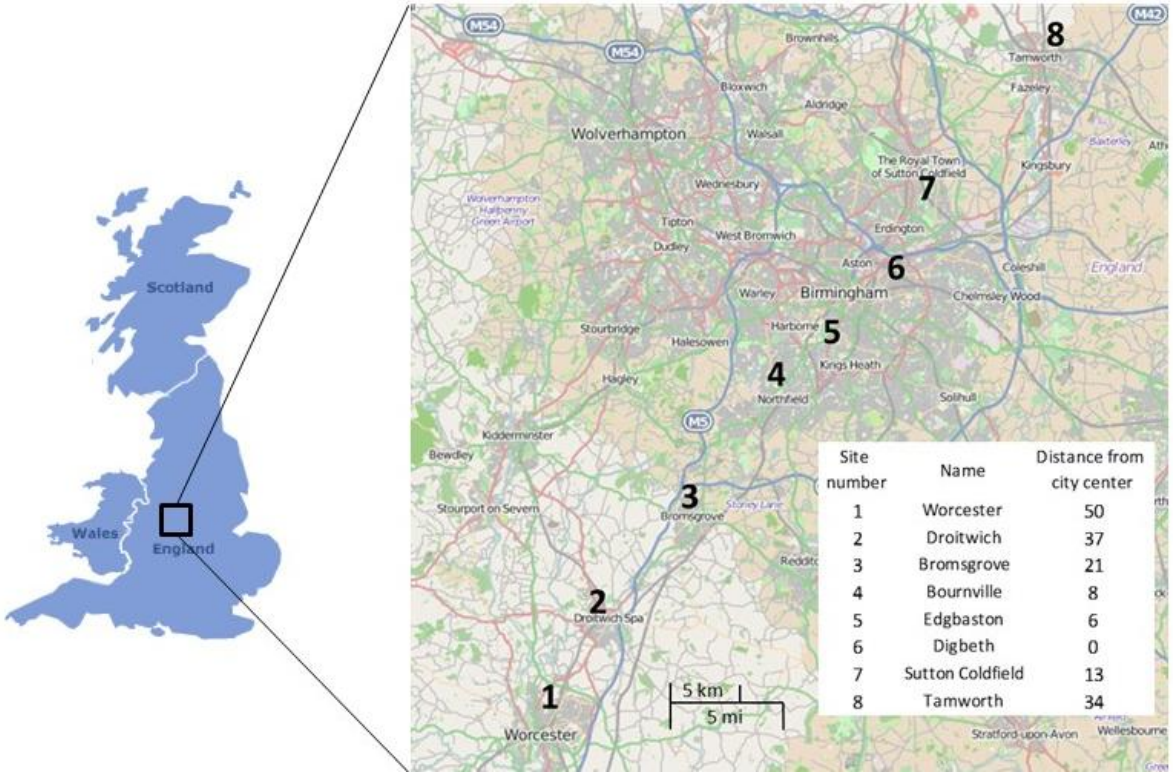

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608 Figure 1 - Passive air and soil sampling locations for the urban-rural transect.

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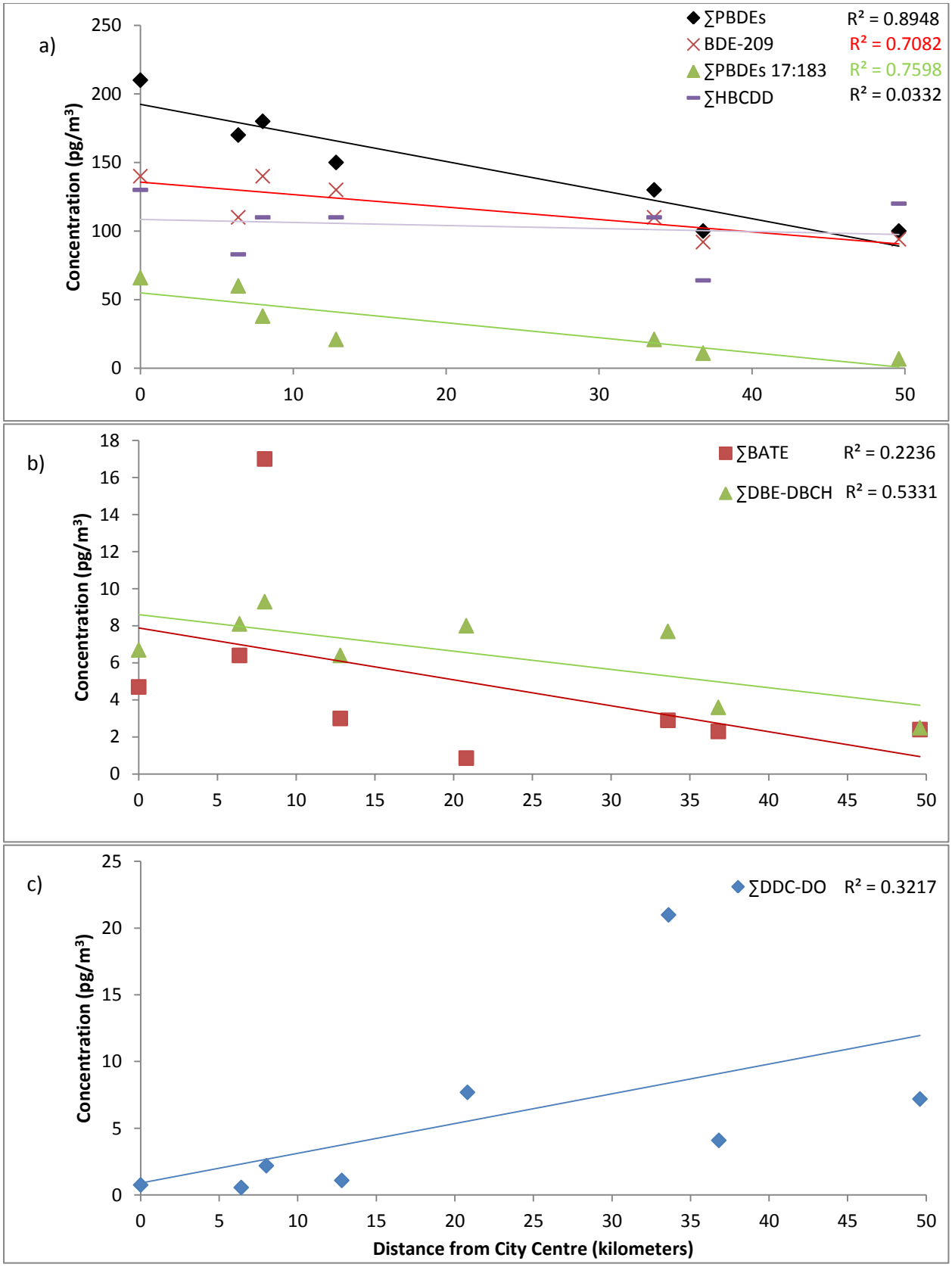

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613 [a](Bromsgrove and August to October samples (all sites) excluded)

614 Figure 2 Correlations between mean concentrations and distance from city centre for a) BDE-
615 209[a], ΣPBDEs[a] , $\Sigma PBDEs_{17:183}$[a] and ∑HBCDD, b)∑BATE and ∑DBE-DBCH; and c) ∑DDC-
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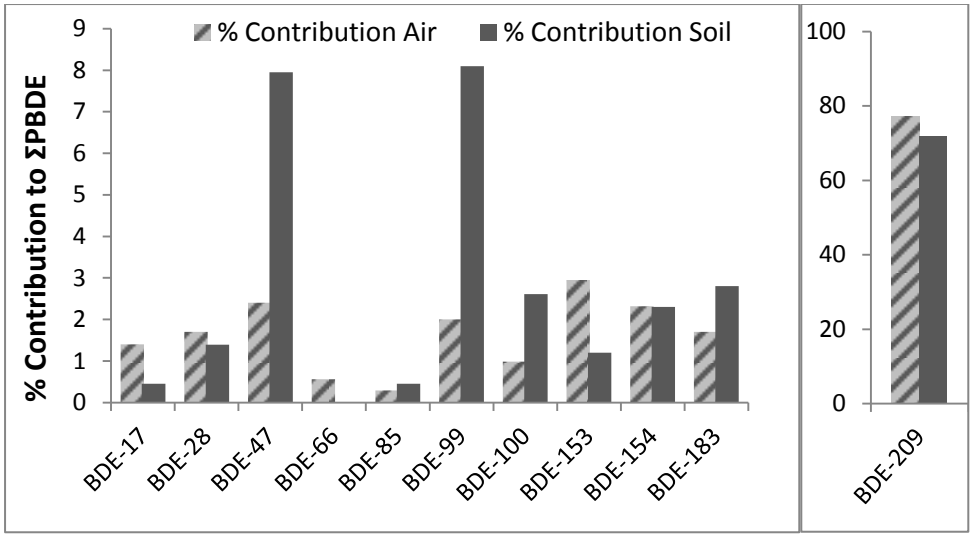

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620 Figure 3 - Mean PBDE congener profile of all soil and air samples for all sites along the
621 rural-urban transect in the West Midlands, UK. n=48 for air samples, n=8 for soil sample

Table 1 – Mean (±standard deviation) concentrations (pg m^{-3}) of selected PBDEs and EFRs in air for each sampling site. "<" indicates a compound was below the detection limit.

Location	Site #	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	∑PBDEs	∑tri-hepta PBDEs	∑HBCDD	BATE	∑DDC-DO	∑DBE-DBCH
Worcester	**1**	1.2 ± 1.4	1.8 ± 1.3	0.62 ± 1.4	0.53 ± 0.83	0.67 ± 0.96	0.92 ± 0.99	<1.5	94 ± 99	100 ± 97	6.8 ± 3.2	120 ± 120	2.4 ± 1.9	7.2 ± 16	2.5 ± 3.5
Droitwich	**2**	2.0 ± 2.0	1.6 ± 2.1	0.22 ± 0.48	<0.45	1.6 ± 3.5	1.5 ± 3.2	1.8 ± 4.1	92 ± 130	100 ± 130	11 ± 16	64 ± 69	2.3 ± 1.5	4.1 ± 7.6	3.6 ± 5.5
Bromsgrove	**3**	3.6 ± 3.4	4.9 ± 6.0	6.0 ± 13	2.5 ± 5.6	6.5 ± 11	4.1 ± 7.3	4.8 ± 11	370 ± 520	490 ± 590	37 ± 65	95 ± 95	0.86 ± 1.2	7.7 ± 12	8.0 ± 15
Bournville	**4**	3.7 ± 2.3	5.2 ± 3.6	3.5 ± 4.8	1.9 ± 3.7	5.9 ± 9.4	3.8 ± 6.6	4.9 ± 7.9	140 ± 170	180 ± 150	38 ± 47	110 ± 140	17 ± 9.4	2.2 ± 3.0	9.3 ± 14
Edgbaston	**5**	5.4 ± 9.3	7.6 ± 11	7.5 ± 16	5.2 ± 11	11 ± 23	12 ± 20	<1.5	110 ± 92	170 ± 100	60 ± 110	83 ± 90	6.4 ± 5.8	0.57 ± 0.81	8.1 ± 12
Digbeth	**6**	5.9 ± 9.1	7.9 ± 9.0	6.0 ± 9.6	2.4 ± 5.2	14 ± 25	8.4 ± 15	11 ± 21	140 ± 120	210 ± 110	66 ± 110	130 ± 130	4.7 ± 3.9	0.76 ± 0.86	6.7 ± 5.5
Sutton Coldfield	**7**	1.7 ± 1.3	3.1 ± 2.6	3.0 ± 3.9	0.53 ± 0.77	2.5 ± 4.1	4.5 ± 5.4	2.8 ± 6.3	130 ± 130	150 ± 130	21 ± 22	110 ± 110	3.0 ± 2.6	1.1 ± 1.3	6.4 ± 12
Tamworth	**8**	2.8 ± 3.3	5.1 ± 4.4	3.9 ± 3.7	2.0 ± 2.9	3.0 ± 5.1	0.37 ± 0.82	<1.5	110 ± 150	130 ± 140	21 ± 19	110 ± 110	2.9 ± 2.9	21 ± 46	7.7 ± 10

Table 2 – Concentrations of selected PBDEs and EFRs in soil (ng g^{-1} organic matter).

Location	Site #	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	∑PBDEs	∑tri-hepta PBDEs	ATE	∑DDC-CO	DBDPE
Worcester	**1**	0.18	0.68	0.58	0.19	<0.15	<0.12	<0.19	1.5	3.6	2.1	0.076	1.2	0.21
Droitwich	**2**	0.085	0.58	0.55	0.12	<0.082	<0.064	<0.11	0.94	2.3	1.4	0.30	<0.016	<0.022
Bromsgrove	**3**	<0.026	2.1	1.6	0.45	<0.13	<0.10	<0.17	45	49	4.2	0.10	2.1	0.34
Bournville	**4**	0.50	0.95	0.77	0.26	0.30	1.6	<0.11	1.7	6.2	4.4	0.47	1.4	0.35
Edgbaston	**5**	0.26	0.84	0.95	0.31	0.28	0.28	0.62	5.7	9.4	3.7	0.045	1.9	0.36
Digbeth	**6**	0.31	1.4	1.1	0.31	0.44	<0.077	1.6	15	21	5.8	0.18	4.5	0.62
Sutton Coldfield	**7**	<0.0085	0.76	0.88	0.51	<0.043	<0.034	<0.056	8.7	11	2.2	0.010	2.0	0.15
Tamworth	**8**	0.14	1.9	1.5	0.15	0.18	0.28	0.76	10	15	4.9	0.69	2.0	0.99

Supplementary Material

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